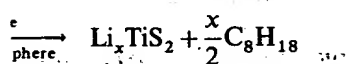


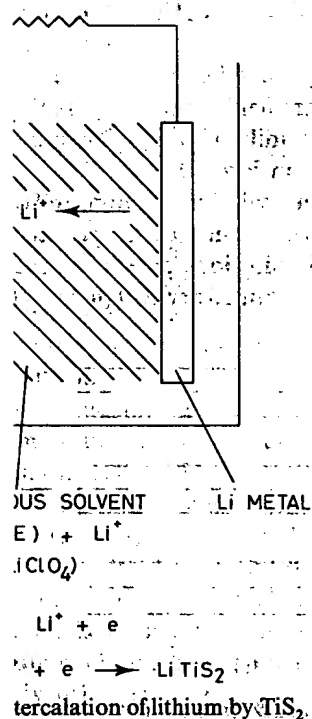
Exhibit A

The reaction is usually carried out in an anhydrous solvent as the source of lithium:



at room temperature and the Li_xTiS_2 solid is formed with hexane. *n*-Butyl lithium is a very mild reducing agent; agents which have a higher reduction potential will further reduce the chalcogenide to give lower chalcogenides or even elemental chalcogen.

An electrochemical method, shown in Fig. 2.10, involves bonding the Li_xTiS_2 solid to a metal grid with a Li^+ -containing electrolyte, e.g. LiClO_4 in dioxolane. A sheet of lithium metal is used as the anode. On closing the external circuit, an electron current flows in the external circuit from the anode, through the electrolyte, to the cathode (TiS_2). The rate of intercalation and its stoichiometric x value may be controlled by the potential of the cell. Prior to reaction, the cell shown in Fig. 2.10 has a potential of ~ 2.5 V and this gives the Li/TiS_2 cell.



couple considerable potential for energy storage (see Chapter 13). A battery constructed in this way has three to four times the energy stored in a lead-acid battery of the same weight.

The two methods described for the synthesis of Li_xTiS_2 are typical of a large variety of possible intercalation reactions. By such methods it is possible to intercalate other alkali cations, Cu^+ , solvated ions, Ag^+ , H^+ , NH_3 , organic amines (i.e. molecules that can donate electrons and therefore act as Lewis bases) and metallocenes. Also, a large number of layered and tunnel compounds are capable of intercalation. As well as graphite and the disulphides and diselenides of many transition metals, the list includes $\text{Ta}_2\text{S}_2\text{C}$, NiPS_3 , FeOCl , V_2O_5 , MoO_3 , TiO_2 , MnO_2 , WO_3 , etc. A particularly well-known example, which is not discussed further here, is the formation of tungsten bronzes, e.g. Na_xWO_3 , by reaction of WO_3 and sodium metal.

2.4.3 Ion exchange reactions

In structures which contain, for instance, an anion array that has open layers or interconnected channels, it may be possible to replace some of the cations by ion exchange and thereby synthesize new compounds. This has been done in the β -alumina family of compounds, whose layered structure is shown schematically in Fig. 2.11. The structure consists of 'spinel blocks', approximately 9 Å thick, that are separated from each other by relatively open 'conduction planes'. These conduction planes contain (a) bridging oxygen atoms that act as props between the spinel blocks and (b) Na^+ ions which are mobile and impart to β -alumina its solid-electrolyte properties. By immersing β -alumina in suitable molten salts at, for example, 300°C, it is possible to ion-exchange Na^+ for a large variety of cations such as Li^+ , K^+ , Rb^+ , Ag^+ , Cu^+ , Tl^+ , NH_4^+ , In^+ , Ga^+ , NO^+ , and H_3O^+ . More recently, it has been found that divalent cations such as Ca^{2+} may enter the conduction planes by immersing in molten salts at 600 to 800°C (to maintain electroneutrality, each Ca^{2+} replaces two Na^+ ions). The extent of the ion exchange under equilibrium conditions depends on the melt composition, as

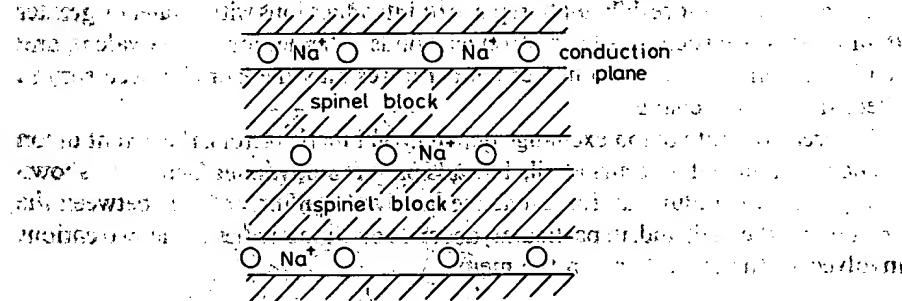


Fig. 2.11. Schematic layered structure of β -alumina of approximate composition $\text{Na}_2\text{O} \cdot 8\text{Al}_2\text{O}_3$.

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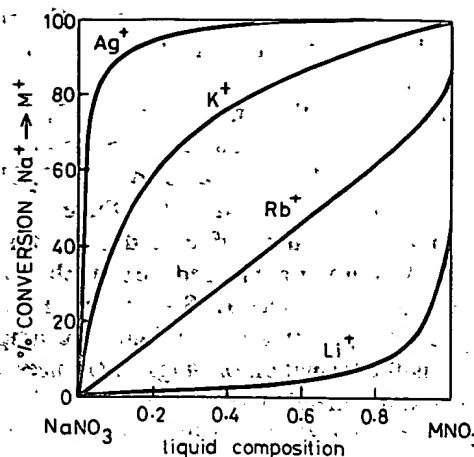


Fig. 2.12 Equilibria between β -alumina and binary nitrate melts at 300 to 350 °C. (From Yao and Kummer, 1967)

shown in Fig. 2.12 for the equilibria between β -alumina crystals and binary nitrate melts containing NaNO_3 and another metal nitrate at 300 to 350 °C. Thus, it is particularly easy to exchange Na^+ for Ag^+ . Also, it is possible to effect a controlled partial ion exchange by controlling the composition of the nitrate melt. Ion-exchanged β -aluminas may also be prepared by electrochemical methods, similar to those described in the preceding section.

Ion-exchange reactions have been studied in considerable detail in β -alumina, but the same principles could probably be applied to a wide variety of crystals, especially alkali-containing crystals. Ion exchange reactions are constrained by both kinetic and thermodynamic factors. Kinetic factors are influenced largely by the mobility of ions: at elevated temperatures, e.g. $\sim 300^\circ\text{C}$, alkali ions are often quite mobile in crystals and are capable of ion exchange on immersion in a suitable melt. Thus, $\text{Ag}_2\text{Si}_2\text{O}_5$, which has a silicate sheet structure, has been prepared by immersing $\text{Na}_2\text{Si}_2\text{O}_5$ crystals in molten AgNO_3 at 280 °C. However, it is considerably more difficult to replace or introduce ions with a valency greater than unity since such ions form stronger bonds, whether ionic or covalent, and tend to be immobile. Much higher temperatures may therefore be necessary to effect their ion exchange.

Whereas the rate of ion exchange depends on kinetic factors, the extent of ion exchange, if indeed it occurs at all, depends on thermodynamic factors, as shown in Fig. 2.12 for β -alumina. Ion exchange involves equilibria of ions between the crystal and the melt and, in particular, depends on the activities of the two cations involved in the crystal and in the melt.

2.4.4 Synthesis of new metastable phases by 'Chimie Douce'

The precursor methods described in Sections 2.1.3 and 2.1.4 have the advantage that reaction takes place at much lower temperatures than when using

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